DETERMINATION OF THE ELASTIC CONSTANTS OF TETRAGONAL (4, 4, 4/m) CRYSTALS FROM THE STUDY OF DIFFUSE X-RAY REFLECTIONS

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ABSTRACT. Theoretical relationships connecting diffusely scattered X-ray intensities from crystals with its elastic constants have been derived for tetragonal crystals of classes 4, 4 and 4/m. Methods of evaluation of all the seven elastic constants for these types of crystals from a quantitative measurement of diffuse X-ray scattering only, have been described and the results are being used to determine elastic constants of single crystals of Penta-erythritol (Tetragonal 4)

The elastic properties of tetragonal crystals belonging to the point groups 4, $\bar{4}$, 4/*m* are defined by the matrix (according to the classical theory of elasticity)

$$
\begin{matrix}
C_{12} & C_{13} & 0 & 0 & C_{1} \\
C_{11} & C_{13} & 0 & 0 & -C \\
 & C_{33} & 0 & 0 & 0 \\
 & & C_{44} & 0 & 0 \\
 & & & C_{44} & 0 \\
 & & & & C_{66}
\end{matrix}
$$

where C_{11}, etc are the elastic constants of the crystal.

The relations for the evaluation of the elastic constants of the tetragonal crystals of more symmetrical point groups (namely, 42, $\bar{4}$2m, 4/mmm) from the intensity measurement of thermal diffuse scattering of X-rays, have been derived by Prasad and Wooster (1955) The intensity of diffuse X-ray scattering (1st order only) from a small element of volume of the crystal along a line passing through a reciprocal lattice point (*hkl*) which is responsible for the diffuse scattering, is proportional to the value of the expression $K[uvw]_{hkl}$ (designated as rekha constant by Ramchandran and Wooster, 1951)
where,

$$K[uvw]_{hkl} = L^2A^{-1}{}_{11} + M^2A^{-1}{}_{22} + N^2A^{-1}{}_{33} + 2MNA^{-1}{}_{23} + 2NLA^{-1}{}_{31} + 2LMA^{-1}{}_{22}$$

where L, M, N, are the direction cosines of the reciprocal lattice vector with respect to the crystal axes (the elastic axes also coincide with the crystal axes for these cases) and u, v, w are the direction cosines of the thermal wave vector and A^{-1}_{11} etc. are the elements of the matrix inverse to the matrix A_{ij} whose elements for tetragonal crystals of classes 42, $\bar{4}2m$ 4mm and 4/mmm are given by

$$
\begin{aligned}
A_{11} &= C'_{11}u^2+C'_{66}v^2+C'_{44}w^2 \\
A_{22} &= C'_{66}u^2+C'_{11}v^2+C'_{44}w^2 \\
A_{33} &= C'_{44}(u^2+v^2)+C'_{33}w^2 \\
A_{23} &= vw(C'_{44}+C'_{13}) \\
A_{31} &= wu(C'_{44}+C'_{13}) \\
A_{12} &= vu(C'_{66}+C'_{12})
\end{aligned}
$$

Prasad and Wooster have also indicated that for very simple and elementary directions of the reciprocal lattice vector and the thermal wave vector, the values of $K\,|u, v, w]_{hkl}$ depend on one or two elastic constants only. Consequently, in principle, all the elastic constants can be evaluated without difficulty from the measurements of the intensities of the diffusely scattered X-rays along these directions. Since $C'_{16} = -C'_{26} \neq 0$ for the crystal classes which have been dealt with in this paper (whereas $C'_{16} = C'_{26} = 0$ for the classes considered by Prasad and Wooster) the values of $K|uvw]_{hkl}$ involve many elastic constants even for simple reciprocal lattice vectors and simple directions of thermal wave vectors. Hence determination of all the elastic constants from X-ray measurements is apparently quite difficult, as will be evident from the succeeding text where the relationships and the method to be applied in such cases have been described. It can be shown that the elements of the matrix A_{ij} for tetragonal crystals of classes 4, $\bar{4}$, and 4/m are given by .

$$
\begin{aligned}
A_{11} &= C'_{11}u^2+C'_{66}v^2+C'_{44}w^2+2uvC'_{16} \\
A_{22} &= C'_{66}u^2+C'_{11}v^2+C'_{44}w^2-2uvC'_{16} \\
A_{33} &= C'_{44}(u^2+v^2)+C'_{33}w^2 \\
A_{23} &= vw(C'_{44}+C'_{13}) \\
A_{31} &= wu(C'_{44}+C'_{13}) \\
A_{12} &= (u^2-v^2)C'_{16}+uv(C'_{66}+C'_{12})
\end{aligned}
$$

Values of the $K|uvw]_{hkl}$ derived for the present cases for some reciprocal lattice points and some simple directions of propagation of the thermal waves are given in Table I.

It can be seen from Table I that the constants C_{44} and C_{33} can be determined independently from observations along $[001]_{h00}$ and $[001]_{00l}$ yielding the values

TABLE I

K values for the tetragonal crystal classes (4, $\bar{4}$ and $4/m$)

Direction cosines (u,v,w) of the direction of propagation of the thermal wave.	Index of the reciprocal lattice points hoo	ool	hho	hol
100	$\left[C_{66}/(C_{11}C_{66}-C_{16}^2)\right]$	$1/C_{44}$	$\left[\dfrac{L^2C_{66}+M^2C_{11}-2LMC_{16}}{(C_{11}C_{66}-C_{16}^2)}\right]$	$\left[L^2C_{66}/(C_{11}C_{66}-C_{16}^2)+N^2/C_{44}\right]$
010	$\left[C_{11}/(C_{11}C_{66}-C_{16}^2)\right]$	$1/C_{44}$	$\left[\dfrac{(L^2C_{11}+M^2C_{66}+2LMC_{16})}{(C_{11}C_{66}-C_{16}^2)}\right]$	$\left[L^2C_{11}/(C_{11}C_{66}-C_{16}^2)+N^2/C_{44}\right]$
001	$1/C_{44}$	$1/C_{33}$	$(L^2+M^2)/C_{44}$	$\left[L^2/C_{44}+N^2/C_{33}\right]$
$\left(\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right)$	$\dfrac{2[(C_{66}+C_{44})(C_{44}+C_{33})]}{\Delta}$	$\dfrac{2[(C_{66}+C_{44})(C_{44}+C_{11})-C_{16}^2]}{\Delta}$		$L^2K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{hoo} - N^2K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{ool} + \dfrac{4NL(C_{44}+C_{13})(C_{44}+C_{33})}{\Delta}$
$\left(-\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right)$ or $\left(\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right)$	"	"		$L^2K\left[-\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{hoo} + N^2K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{ool} - 4NL\dfrac{(C_{44}+C_{13})(C_{44}+C_{33})}{\Delta}$

where $\Delta = [(C_{44}+C_{11})(C_{66}+C_{44})(C_{44}+C_{33}) - C_{16}^2(C_{44}+C_{33}) - (C_{44}+C_{13})^2(C_{66}+C_{44})]$

TABLE I (*contd.*)

K values for the tetragonal crystal classes (4, $\bar{4}$ and 4/*m*)

Direction cosines (u,v,w) of the direction of progration of the thermal wave.	Index of the reciprocal lattice points			
	hoo	*ool*	*hko*	*hol*
$\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$	$\left[\frac{2(C_{66}+C_{11}}{C_{11}^2+2C_{66}} \frac{-2C_{16})}{(C_{11}-C_{12})-C_{12}^2-4C_{16}^2}\right]$	$1/C_{44}$		
$\left(-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)$ or $\left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right)$	$\left[\frac{2(C_{66}+C_{11}}{C_{11}^2+2C_{66}} \frac{-2C_{16})}{(C_{11}-C_{12})-C_{12}^2-4C_{16}^2}\right]$	$1/C_{44}$		
$\left(0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)$ or $\left(0, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)$ or $\left(0, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}\right)$	$\frac{2[(C_{44}+C_{33})(C_{11}+C_{44}) - (C_{44}+C_{13})^2]}{\Delta}$	$\frac{2[(C_{66}-C_{44})(C_{11}+C_{44})-C_{16}^2)]}{\Delta}$		

where $\Delta=[(C_{44}+C_{11})(C_{66}-C_{44})(C_{44}+C_{33})-C_{16}^2(C_{44}+C_{33})-(C_{44}-C_{13})^2(C_{66}-C_{44})]$

of $K[001]_{hoo}$ and $K[001]_{ool}$ respectively. The value of C'_{44} can also be evaluated from observations along [001] for different (hko) reciprocal lattice nodes and also from $K(010)_{001}$. Further, the values of C'_{44} and C'_{33} can be simultaneously obtained from observations along [001] for at least two different (hol) reciprocal lattice nodes. Since such determined values of C'_{44} and C'_{33} are dependent on two observed K-values, its accuracy of determination is theoretically less than that mentioned at the beginning. Again, by substituting the value of C'_{44} in the observed value of $K[001]$, the value of C'_{33} can be determined easily considering one (hol) reciprocal lattice node only at a time. To increase the accuracy of thus determined value of C'_{33}, we are to choose a reciprocal lattice node for which the value of L is very low compared to that of N, i.e. a node whose l index is much higher than its h index; in such condition the value of $K[001]_{hol} = [L^2/C'_{44} + N^2/C'_{33}]$ will be guided primarily by the value of N^2/C'_{33}. The value of C'_{44} can further be determined by combining the observed value of $K[100]_{hol}$ with $K[100]_{hoo}$ and $K[010]_{hol}$ with $K[010]_{hoo}$. Alternatively, by substituting the value of C'_{44} in $K[100]_{hol}$ and $K[010]_{hol}$, the values of $\frac{C'_{66}}{(C'_{11}C'_{66}-C'^2_{16})}$ and $\frac{C'_{11}}{(C'_{11}C'_{66}-C'^2_{16})}$ can be obtained respectively from which we can get the ratio C'_{11}/C'_{66}. It will be seen further that solution of more than one relation only gives the values of the ratio of the constants (viz. C'_{11}/C'_{66}, etc.) and C'_{11}, C'_{66} and C'_{16} cannot be determined independently and directly. For determining the absolute values of these three constants, the method of successive approximation suggested is as follows :

From the Table I, we have

$$\frac{1}{K[100]_{hoo}} = \left(C'_{11} - \frac{C'^2_{16}}{C'_{66}} \right) \quad \ldots \quad (1)$$

$$\frac{1}{K[010]_{hoo}} = \left(C'_{66} - \frac{C'^2_{16}}{C'_{11}} \right) \quad \ldots \quad (2)$$

and

$$K[100]_{hko} = \frac{(L^2C'_{66} + M^2C'_{11} - 2MLC'_{16})}{C'_{11}/K[010]} \quad (3)$$

Substituting the experimentally determined values of $1/K[100]_{hoo}$ and $1/K[010]_{hoo}$ for C_{11} and C_{66} respectively in the relation (3), we can thus get some value for C_{16}. Let us now substitute in relation (1) this value of C'_{16} along with the experimentally determined value of $1/K[010]$ for C_{66}. We thus get some value for C_{11}. These values of C_{11} and C_{16} may be substituted in the relation (2) to give a better value for C_{66}. These values of C'_{11} and C_{66} can now be substituted in relation (3) to yield a better value for C_{16}. This value for C_{16} and C_{66} on substitution in relation (1) gives a better value for C_{11} and so on. We can in this way go on repeating the process again and again till further refinements do not change the values of C_{11}, C_{66} and C_{16}. The smaller the value of C_{16} as compared to C_{11}, and C_{66}, the lesser would be the number of repetitions needed. It should be remarked that this method of successive approximation does not assume anything regarding the relative values of the constants involved. Actually a numerical example assuming tentatively $C_{11} = 2C_{66} = 4C_{16}$ required about four repetitions whereas in another example in which $C_{11} = 2C_{66} = 2C_{16}$, about eight repetitions were found to suffice. In fact the constant C_{16} relates an external stress to shear strain, therefore it would be expected for most of the cases to be smaller than the constants C_{44}, C_{55}, C_{66} which relate a shear stress to a shear strain in the same plane and considerably smaller than the constants C_{11}, C_{22}, C_{33} which relate an extentional stress to a collinear extentional strain. So in general not many repetitions will be required for getting the correct value of C_{11}, C_{66}, and C_{16}. Since we are to use three observational intensities each of which depends on these constants namely, C_{11}, C_{66} and C_{16} the values of C_{11}, C_{66}, C_{16} will be theoretically less accurate than the values of the constants C_{44} and C_{33} which have been derived from intensities depending on one constant only. But in practical cases, the determination of a particular elastic constant derived by using different value of $K|u, v, w|_{hkl}$, $K|u', v', w'|_{h'k'l'}$ does not appreciably reduce the accuracy of its determination. Once we obtain the absolute values of the constants C_{11} and C_{66} by substituting the value of C_{11} in the ratio C_{11}/C_{66} which is obtained from different sources (as mentioned earlier), the value of C_{66} can be determined or vice versa. The constant C_{16} with proper sign can also be evaluated from the observed value of

$$\frac{K\left[\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right]_{hoo}}{K\left[-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right]_{hoo} \text{ or } K\left[\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right]_{hoo}} = \frac{(C_{11}+C_{66}-2C_{16})}{(C_{11}+C_{66}+2C_{16})}$$

when the values of C_{11} and C_{66} are substituted there. Similarly from observations

$$\left[\frac{K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{hol}}{K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{hol} \text{ or } K\left[\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right]_{hol}}\right]$$

one obtains the value of the ratio

$$\frac{L^2[(C_{66}+C_{44})(C_{44}+C_{33})]+N^2[(C_{55}+C_{44})(C_{44}+C_{11})-C_{16}^2]+2LN(C_{44}+C_{33})(C_{33}+C_{13})}{L^2[(C_{66}+C_{44})(C_{44}+C_{33})]+N^2[(C_{66}+C_{44})(C_{44}+C_{11})-C_{16}^2]-2LN(C_{44}+C_{33})(C_{33}+C_{13})}$$

which, when the values of C_{11}, C_{33}, C_{44}, C_{66} and C_{16} are substituted, gives the value of C_{13} with proper sign. Again, if we substitute the values of C_{11}, C_{33}, C_{66}

and C_{16} in the observed values of $K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{hoo}$, $K\left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{ool}$

$K\left[0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right]_{hoo}$ and $K\left[0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right]_{ool}$ each of which gives a second degree equation in C_{13} and retain only the positive value of the solution under the surd, the value of the constant C_{13} can be evaluated with proper sign. The remaining constant C_{12} can be determined from the observed values of $K\left[\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right]_{hoo}$

and $K\left[\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right]_{hoo}$ or $K\left[-\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]_{hoo}$ each of which gives a second degree equation in C_{12} on substitution of the values of C_{11}, C_{66} and C_{16}; retaining only the positive values of the solution under the surd C_{12} with proper sign can be evaluated. Other more complex directions of observations can be taken for which K values depend on C_{12} in combination with the other constants and C_{12} can be evaluated from those expressions just proceeding in the same manner as before.

The relations derived and the method of evaluation of the elastic constants indicated above are being used for the determination of the seven elastic constants (C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, C_{13} and C_{16}) of crystals of Pentaerythritol (Point Group 4) using the photographic method as developed by Chakraborty and Sen (1958) and the complete experimental results will be published in near future

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